

A NEW CLASS OF WATER DISPERSIONS RESISTANT TO FREEZING-THAWING

L.S. Podenko, N.S. Molokitina, V.V. Shalamov

*Institute of Earth's Cryosphere, Siberian Branch of the Russian Academy of Sciences,
PO box 1230, Tyumen, 625000, Russia; lpodenko@yandex.ru*

A new class of water dispersions has been obtained through encapsulation by silica nanoparticles with polyvinyl alcohol. This form is more stable than the previous ones against freeze-thaw cycles. The new systems are advantageous over dry water in stability and contents of liquid water, being similar to the latter in the degree of liquid phase dispersion.

Hydrophobic silica nanoparticles can stabilize disperse systems consisting of fine water drops (so-called powdered or dry water) [Schutte and Schmitz, 1968]. Dry water behaves as powder, is free-flowing, and contains up to 98 wt.% liquid phase. As it has been shown recently, gas hydrate formation with dry water is faster than with bulk water or crushed ice [Wang et al., 2008; Carter et al., 2010]. The acceleration of gas hydrate formation with the use of dry water stabilized by hydrophobic nanoparticles is relevant to the technologies of natural gas transportation and storage in the hydrate form [Gudmundson et al., 2000; Kanda et al., 2005; Watanabe et al., 2008].

Dispersion of water and aqueous solutions in the presence of hydrophobic silica nanoparticles may lead to water encapsulation [Forny et al., 2009]. Such systems of encapsulated water are of broad use in petroleum chemistry, medicine, and biotechnologies [Solodovnik, 1980]. The low-temperature applications require systems stable against freezing-thawing cycles.

Earlier we showed [Podenko et al., 2010] that dry water subjected to freezing and thawing becomes layered as water drops coalesce with one another. Carter et al. [2010] obtained a "dry gel" modification of dry water, which is stable against water phase change, by adding gellan gum (an aqueous solution of polysaccharide) instead of water. Note that this technique requires large amounts of the polymer (20 wt.%) and much energy for powdering the highly viscous gel.

We have investigated the feasibility of using polyvinyl alcohol (PVA) for increasing the stability of disperse systems encapsulated by silica nanoparticles. The PVA polymer was chosen for the capability of its aqueous solutions to form heterogeneous gels as a result of freezing-thawing cycles (cryogels) [Lozinsky, 1998]. The structure of the obtained disperse systems was analyzed by means of optical microscopy and proton magnetic resonance spectroscopy on a Niumag MicroMR NMR pulsed relaxometer, operated at the resonance frequency 20 MHz, following the procedure reported in [Podenko et al., 2010].

The study included experiments on dispersing the PVA solution in the presence of hydrophobic silica nanoparticles (aerosil R 202). For this purpose, a mixture of 95 wt.% PVA aqueous solution (State Standard 10779-78) and 5 wt.% nanometer powder aerosil R 202 was stirred for 60 s at a blender speed of 18,750 revolutions per minute; the concentration of the polymer was 5 wt.%. Gel formation was catalyzed with 1 wt.% boric acid. The viscosity of the starting water gels did not exceed 40 mm²/s.

The resulting water dispersion of PVA (PVA dispersion) had a consistency of paste (unlike the powdery dry water we obtained at the same dispersion conditions). The PVA dispersion had its density almost 1.5 times higher than the apparent density of dry water (0.86 against 0.53 kg/l) approaching the density of 5 % PVA (0.98 g/l). Therefore, the dispersion contained ~84 vol.% PVA solution. According to optical microscopy (Fig. 1), the disperse phase of the obtained system consisted of micron-size drops and their aggregates.

The greater density of the PVA dispersion is evidence of a more compact arrangement of drops in it relative to dry water. The reason of the difference

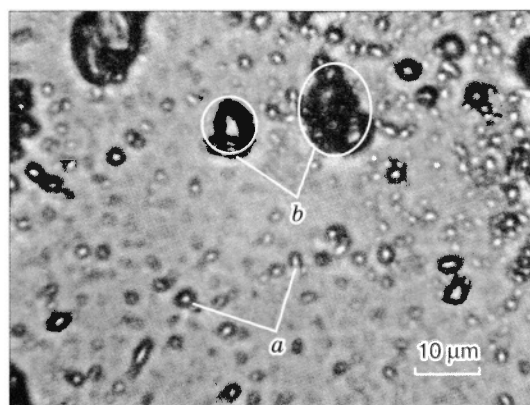


Fig. 1. Polyvinyl alcohol (PVA) dispersion.
a – individual particles, b – aggregates of particles.

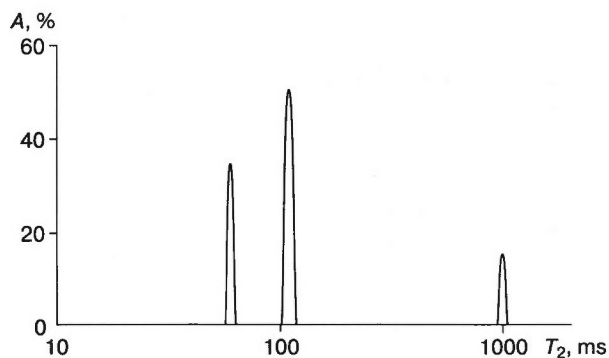


Fig. 2. Distribution (A) of spin-spin relaxation (T_2) of PVA dispersion at 32 °C.

may be as follows. The disperse drops in dry water are stabilized by self-assembling hydrophobic silica (aerosil) nanoparticles which provide its flowability, i.e., low apparent density [Forny *et al.*, 2007]. Polyvinyl alcohol is a high-molecular surfactant [Lozinsky, 1998] and becomes adsorbed on the surfaces of aerosol particles thus preventing them from assembling and formation of a large spatial network. As a result, the polymer drops become stabilized by particles of much smaller sizes, which provides very high concentrations of drops in the disperse system.

The obtained PVA dispersions were investigated in terms of their structure and stability against freezing-thawing cycles in the respective experiments in a liquid cryostat. The temperature schedule was as follows: first the liquid was cooled at 0.5 °C/min from $T_{wf} = 25$ °C to $T_{wf} = -15$ °C (T_{wf} is working fluid temperature), and then heated at the same rate back to $T_{wf} = 25$ °C. The samples were placed in test tubes 10 mm in diameter; the sample temperature (T_{sm}) was monitored with a thermocouple placed in the same tubes.

The data were plotted in a T_{wf} vs. T_{sm} thermogram. The samples showed a crystallization peak at $T_{wf} \sim -12$ °C while cooling and a melting peak at $T_{wf} > -0.5$ °C while heating. Unlike dry water [Podenko *et al.*, 2010], the freezing-thawing cycles caused no stratification in PVA dispersion, i.e., the solution remained disperse after freezing and thawing.

The structure of PVA dispersions was analyzed from their patterns of spin-spin relaxation times (T_2) (Fig. 2). The T_2 pattern, like in the case of dry water, consisted of three relaxation components (Fig. 2), which indicates polydisperse size distribution of drops. We estimated the drop sizes from the parameters of T_2 distribution according to the technique reported in [Podenko *et al.*, 2010]. We found out that ~ 10 μm drops and/or their agglomerates constituted 15% of the PVA solution, and the other drops were ~ 2 μm . Note that the percentage of ~ 10 μm drops and/or their agglomerates decreased about five-fold

after a freezing-thawing cycle, while the other drops grew to only ~ 3 μm , i.e., no relatively large water drops have formed.

Therefore, the presence of PVA in a disperse system increases its freezing-thawing stability. The mechanism of this stabilization may consist in increasing mechanic stability of individual drops as they develop a polymer cryogel structure.

Thus, a new class of water dispersions has been obtained through encapsulation by hydrophobic silica nanoparticles with polyvinyl alcohol. The new systems are advantageous over dry water being easy to obtain, high in liquid water phase (84 vol.%), and stable against freezing and thawing. The latter property allows using PVA dispersions at subzero temperatures.

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